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(19)



(54) COATING COMPOSITION

(71) We, HOECHST AKTIENGESellschaft, a Body Corporate organised under the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions containing binders based on hardenable polyesters.

Thermohardenable binders for powder coating compositions have been described based on combinations of blocked diisocyanates and polyester resins. Such binders have in general good flow properties, good chemical resistance and a high resistance to weathering. The polyester resins used generally contain free hydroxyl groups in addition to ester groups and optionally also ether and urethane groups. The blocked isocyanates usually used are aromatic and aliphatic polyisocyanates wherein some or all of the isocyanate groups present are blocked by compounds containing acidic hydrogen atoms, for example oximes, phenolic compounds and lactams. Analogously, other polycondensation or polymer resins may be used instead of the polyester resins, provided that they contain free hydroxyl groups.

Coatings obtained from these powder coating compositions, for example by electrostatic spraying and hardening, having the disadvantage that their elasticity and, in particular, their impact strength do not satisfy the normal requirements of stoving enamels for practical application. Thus their uses are limited.

Attempts to bring about a substantial increase in elasticity by altering the chemical structure of the synthetic resins containing hydroxyl groups, or by increasing the extent of cross-linking (which can be achieved by increasing the isocyanate content) by using suitable catalysts or by raising the curing temperature having heretofore been unsuccessful.

According to the present invention we now provide a coating composition which comprises a binder comprising A) a reaction product of a hardenable polyester and a partially blocked polyisocyanate (as herein defined) and B) an amount at up to 38.5 per cent by weight (referred to the total amount of component A) of an epoxy resin.

The term "a partially blocked polyisocyanate" used herein refers to a compound containing isocyanate groups, some of which are protected with blocking groups which are capable of being split off at elevated temperatures, preferably at temperatures below 190°C.

Coatings which we have prepared from compositions according to the invention have good mechanical properties, in particular good elasticity and impact strength, and are particularly smooth. They also have the good properties associated with reaction products of polyesters and polyisocyanates. These surprisingly favourable properties cannot be obtained by either increasing the proportion of blocked isocyanate to a polyester resin or by adding an epoxy resin alone to a polyester resin.

Preferred polyesters for use in the compositions according to the invention are prepared by condensation of ortho-, iso- or terephthalic acid, a hydrogenated or substituted phthalic acid, trimellitic acid, pyromellitic acid, maleic acid, fumaric acid, itaconic acid, adipic acid, glutaric acid, or succinic acid, or mixtures thereof, with one or more polyhydric alcohols, for example ethanediol, the propane-, butane-, pentane- and hexanediols and other polyhydric alcohols with saturated or olefinically unsaturated carbon chains with up to 15 carbon atoms, e.g. dimethylolcyclohexane, bis-(4-hydroxycyclohexyl)-methane and-propane, but-2-ene-diol-1,4, glycerol, trimethylol-ethane and-propane and pentaerythritol. Polyesters which contain at least one trifunctional acid and/or alcohol components are particularly preferred. This component is a

determining factor in the degree of cross-linking of the resin. If carboxylic acids or alcohols with a functionality higher than 2 are present, the proportion of these is preferably from 10 to 60, preferably 20 to 50 mol%, referred to the total molar amounts of acid and alcohol components of the polyester resin. The polyesters used for the preparation of the binders according to the invention may if desired be modified by incorporating monocarboxylic acids, for example benzoic acid, p-t-butylbenzoic acid, or aliphatic, saturated or olefinically unsaturated monocarboxylic acids, (e.g. the fatty acids of linseed oil, soya bean oil, castor oil, coconut oil and dehydrated castor oil, stearic acid and oleic acid), or by incorporating aromatic or aliphatic monohydric alcohols, for example ethanol, the propanols, the butanols, the pentanols, the hexanols and cyclohexanol as well as monohydric alcohols with longer carbon chains, (e.g. lauryl alcohol and oleyl alcohol). The proportion of monofunctional acid or alcohol components should advantageously be not more than 30% by weight, preferably up to 15 and in particular up to 5% by weight, based on the total weight of the acid or alcohol component respectively. Polyesters based on terephthalic acid, phthalic acid and isophthalic acid, either alone or in admixture or in admixture with adipic acid, are preferred.

The most preferred polyester resins are those which are almost free from carboxyl groups and contain free hydroxyl groups. The acid number, measured according to DIN standard 53 402, should generally be less than 5, preferably less than 3. It is however also possible to use polyester resins with higher acid numbers, provided that, by a suitable choice of working conditions, steps are taken to make sure that they do not react prematurely with the epoxy groups of the epoxy resins. The hydroxyl numbers of the starting polyesters, determined according to DIN standard 53 240, should appropriately be from 50 to 250, preferably from 100 to 220, and in particular from 130 to 200. The melting points of the polyesters, measured by the capillary method, are generally in the range from 60 to 90°C, preferably from 65 to 80°C. The melting viscosities of the resins, measured at 130°C, are generally from 100 to 7000 poise, and preferably from 100 to 1400 poise. Polyesters with higher melting viscosities, e.g. 1400 to 7000 poise, may be used but a fairly low melting viscosity is generally particularly advantageous for easier processing.

The polyester resins may be prepared according to the conventional working methods for polycondensation resins, e.g. by condensation in a melt, or by esterification with azeotropic distillation of the water formed in the reaction, or by the interchange of ester radicals of high molecular weight polyesters, such polycondensations being advantageously performed under a protective gas atmosphere, e.g. nitrogen or carbon dioxide. At the end of the esterification, which is generally effected at 160 to 250°C, it is advisable to work under reduced pressure, at least for a short period, in order to distil off any unreacted starting materials and low molecular weight reaction products, and to bring the melting point of the polyesters into the preferred range.

Before the reaction with the partially blocked polyisocyanates, further synthetic resins containing hydroxyl groups capable of reacting with isocyanate groups, for example, acrylic and methacrylic copolymers (e.g. hydroxyethyl methacrylate/butyl acrylate/styrene copolymer and methyl methacrylate/hydroxypropyl acrylate/styrene copolymer), vinyl homopolymers and copolymers (e.g. polyvinyl alcohol and saponification products of polyvinyl acetate) and polyurethane resins may if desired be incorporated into the binder or the polyester. The molar proportion of OH groups in these resins is preferably at most equal to the molar proportion of OH groups in the polyester.

Polyisocyanates which may be used include for example the known commercial aromatic, cycloaliphatic and aliphatic, at least bifunctional polyisocyanates, provided that they are at least partially blocked, and condensation products of these isocyanates which still contain free isocyanate groups, for example toluylene diisocyanate; diphenylmethane diisocyanate; phenyl diisocyanate-1,3; isophorone diisocyanate; cyclohexane diisocyanate-1,2; hexane diisocyanate-1,6; 2,2,4- and 2,4,4-trimethylhexane diisocyanate-1,6; 2,4,6-triisocyanatotoluene; 4,4',4''-triisocyanatotriphenylmethane; 2,4,4'-triisocyanatodiphenylmethane; 2,2',5,5'-tetraisocyanatodiphenylmethane; the reaction product of 1 mol of trimethylolpropane with 3 mol of toluylene-2,4-diisocyanate; condensation products containing free isocyanate groups of polyisocyanates and polyhydric alcohols; and the condensation product obtained by reacting 3 mols of hexanediiisocyanate-1,6 with 1 mol of water.

If necessary the free isocyanate groups in the polyisocyanate are at least partially blocked by reaction with a blocking agent, preferably one which forms urethane or urea groups, which can be split off again at elevated temperatures re-forming the isocyanate groups. Blocking agents which may be used are compounds with reactive hydrogen atoms, for example mono- and polyhydric phenols (e.g. 4,4'-dihydroxydiphenylpropane), β -dicarbonyl compounds (e.g. acetoacetic acid esters, malonic acid esters and acetylacetone), carboxylic acid imides (e.g. phthalimide), unsubstituted or N-substituted carboxylic acid amides (e.g. acetanilide), sulphonic acid amides (e.g. benzene sulphonamide) mercapto compounds (e.g. 2-mercaptobenzothiazole), but preferably lactams e.g. ϵ -caprolactam. The free isocyanate groups may be quantitatively or partially reacted with these blocking agents; in the latter case, preliminary reaction of the partially blocked polyisocyanate with the further synthetic resin containing hydroxyl groups is advantageous.

Epoxy resins which may be used include for example commercial aromatic, aliphatic (particularly cycloaliphatic) or heterocyclic polyglycidyl compounds for example triglycidylisocyanurate, and those products which are obtained by polycondensation of 4,4'-dihydroxydiphenylpropane or methane with epichlorohydrin. The use of epoxy resins based on 4,4'-dihydroxydiphenylpropane is particularly advantageous. In order to prevent difficulties in processing, the melting point (as measured by the capillary method) of the epoxy resin used should not be below 70°C, preferably at least 100°C, best of all 120°C or above.

The mixing ratio of the components of the coating composition, viz. the polyester and, if present, the synthetic resin containing hydroxyl groups (I), the blocked polyisocyanate (II) and the epoxy resin (III), can be varied within wide limits, without thereby affecting the improved properties of the hardened coatings therefrom. However, particularly good results are obtained if a) per mol equivalent of hydroxyl groups in (I), there are 0.5 to 1.5, preferably 0.6 to 1.35 and in particular 0.7 to 1 mol equivalents of free and blocked isocyanate groups in (II) and b) per mol equivalent of free and blocked isocyanate groups in (II), there are 0.1 to 1.0, preferably 0.2 to 0.8, best of all 0.3 to 0.7 mol equivalent of epoxy groups in (III).

If polyisocyanates which are only partially blocked and still contain free isocyanate groups are used they are advantageously reacted in a preliminary step with the polyester containing the hydroxyl groups, and the further components are then added. If a fully blocked polyisocyanate is used all the components may be mixed together. The individual components are mixed and homogenised in conventional manner for the preparation of powder coating compositions, appropriately by mixing in a kneader or extruder at elevated temperature. Further conventional additives, for example catalysts for accelerating the addition of isocyanate and/or epoxy resin to the hydroxy groups at the polyester and, if present, the further synthetic resin, pigments, fillers and flow agents, may, if desired be added. Mixing is advantageously effected at a temperature which does not exceed the temperature at which the synthetic resin component containing hydroxyl groups starts to react with the blocked isocyanate or the epoxy resin since otherwise there is a danger of gel formation in the mixture, which might lead to deterioration in the surface quality and other properties of the coatings produced therefrom. In general, it is advantageous not to exceed a processing temperature of 130°C, preferably 120°C and in particular 100°C.

The reaction products according to the invention are in general hard, pulverisable resins which, can be ground and sieved in conventional manner to produce powder resins. The powders thereby produced can be electrostatically applied to suitable substrates, particularly metal workpieces, in a conventional manner, e.g. by whirl-sintering, or from systems containing solvents, e.g. by spraying. The particle size of these powder coating compositions is generally up to 100μ, preferably from 50 to 70μ. The thickness of the coating applied may vary considerably, but is generally up to about 250μ, preferably from 40 to 100 and, in particular, 50 to 80μ, thicker coatings usually being obtained by the whirl-sintering process. The coatings may be hardened by heating for example at 160 to 220°C, preferably 180 to 200°C, for 30 minutes. Smooth, firmly adhering coatings are generally obtained, which are distinguished by particularly good elasticity and impact strength.

The following Examples serve to illustrate the coating compositions according to the invention and articles coated therewith. In the Examples, the melting or softening points were in each case determined by the capillary method, unless otherwise stated. The numerical values given in these Tables for the components of the compositions each represent parts by weight.

Examples

Preparation of the polyester resins

Polyester A 1000 g of the polyethylene terephthalate, 670 g of trimethylolpropane and 44.5 g of phthalic anhydride were heated at 260°C in an atmosphere of carbon dioxide until a clear solution was obtained, and the mixture was refluxed for 3 hours at 240°C, while removing the water which formed. As the temperature fell, ethylene glycol was distilled off under a vacuum of 16 mm Hg until a reaction product was obtained having a softening point of 70 to 73°C; a melting viscosity at 130°C of 7000 P; a hydroxyl number of 180, and an acid number below 2.

Polyester B 3760 g of polyethylene terephthalate and 1270 g of trimethylolpropane were heated at 260°C in an atmosphere of carbon dioxide with stirring until a clear melt was formed. The mixture was then further processed as in A until a product was obtained having a softening point of 67 to 70°C, a melting viscosity at 130°C of 1000 P, a hydroxyl number of 165; and an acid number below 2.

Polyester C The same mixture as in B was processed as in A until a product having a softening point of 78 to 80°C, a melting viscosity of 4000 P at 130°C; a hydroxyl number of 185, and an acid number below 2 was obtained.

Polyester D 6.3 g of ethyl hexyl titanate (a catalyst for the interchange of ester radicals), were added to a mixture of 4200 g of polyethylene terephthalate and 1400 g of trimethylolpropane, and the mixture was heated at 260°C in an atmosphere of carbon dioxide with stirring until a homogeneous melt was formed. After cooling to 240°C, 475 g of isononanoic acid and 183 g of benzoic acid were added, and the mixture was esterified at 220 to 230°C until the acid number was below 3, the water formed being simultaneously distilled off. Finally, the ethylene glycol was

distilled off under a 16 mmHg vacuum until a product having a softening point of 55°C, a melting viscosity of 120 P at 130°C, a hydroxyl number of 130, and an acid number below 2 was obtained.

Polyester E 355 g of phthalic anhydride, 332 g of isophthalic acid, 88 g of adipic acid, 440 g of trimethylolpropane and 250 g of propanediol-1,2 were heated together at 220 to 230°C and the water formed was continuously removed. As soon as an acid number of 5 had been reached, the mixture was further heated under reduced pressure at 200 to 210°C, until a polyester resin formed having a melting point of 58°C, a melting viscosity of 146 P at 130°C, a hydroxyl number of 192, and an acid number below 1.

Polyester F 202 g of phthalic anhydride, 498 g of isophthalic acid, 88 g of adipic acid, 440 g of trimethylolpropane and 250 g of propanediol-1,2 were processed to form a polyester in the same way as described for polyester E. The product had a melting point of 58°C, a melting viscosity of 192 P at 130°C, a hydroxyl number of 207, and an acid number below 2.

Preparation of the blocked polyisocyanates

Isocyanate A = Reaction product of 2 mols of ϵ -caprolactam with 2 mols of isophorone diisocyanate and 1 mol of a dihydric alcohol; isocyanate equivalent weight based on free unblocked isocyanate of 400. The fully blocked isocyanate is sold under the trade name "Adduct B 1065" by Veba Chemie AG, Gelsenkirchen-Bauer, Germany.

Isocyanate B = Addition product of 1.1 mol ϵ -caprolactam and 1 mol isophorone diisocyanate; isocyanate equivalent weight of 173.

Isocyanate C = Reaction product of 1 mol of isophorone diisocyanate, 0.15 mol of trimethylolpropane and 1 mol of ϵ -caprolactam; isocyanate equivalent weight 230; softening point 50 to 55°C.

Isocyanate D = Reaction product of 1 mol of isophorone diisocyanate and 1.1 mol of phenol; isocyanate equivalent weight 162.

The partially blocked isocyanates B, C and D were prepared by heating the isophorone diisocyanate or the mixture of isophorone diisocyanate with trimethylolpropane to 100°C with intensive stirring in a protective gas atmosphere, and subsequently adding the caprolactam or phenol portionwise at temperatures of 100 to 120°C. Since all these products B, C and D still contain free isocyanate groups, in the preparation of powder coating compositions according to the invention, they were subjected to a preliminary reaction, in a melt with the polyester resin being used, until all the free isocyanate groups had reacted.

Epoxy resins

The following commercial products are used as polyfunctional epoxide compounds:

Epoxy resin A = Epoxy resin based on diphenylolpropane and epichlorohydrin, with an epoxy equivalent weight of about 400.

Epoxy resin B = Technically pure triglycidylisocyanurate with an epoxy equivalent weight of 99.

Preparation of powder coating compositions

The polyesters A to F, isocyanates, epoxy resins and other additives were mixed in the proportions indicated in the following Tables either in a heated extruder with subsequent extrusion or in a heatable mixer provided with Z-shaped kneading elements, at 80 to 100°C. Homogeneous, highly viscous melts were obtained. When the melts had cooled to room temperature, they were broken up, ground and sieved to a particle size of less than 100 μ . In the comparison Examples 1, 2, 7, 11, 15, 20 and 23 compositions were produced without epoxy resin and in comparison Example 14 the composition contained no polyisocyanate.

Table 1

Powder compositions I (Example 1)

Example	1 (comparison)
Polyester A	200
Isocyanate A	200
Epoxy resin A	—
dibutyltin dilaurate	2
Silicon-containing flow agent	2.5
TiO ₂	180

Table 2
Powder compositions II (Examples 2 to 6)

Example	2 (comparison)	3	4	5	6
Polyester B	200	200	200	—	200
Polyester C	—	—	—	200	—
Isocyanate B	86	86	86	86	86
Epoxy resin A	—	30	60	110	—
Epoxy resin B	—	—	—	—	15
dibutyltin dilaurate	2	2	2	2	2
Silicon-containing flow agent	2.5	2.5	2.5	2.5	2.5
TiO ₂	125	135	145	170	127

Table 3
Powder compositions III (Examples 7 to 10)

Example	7 (comparison)	8	9	10
Polyester B	200	200	200	200
Isocyanate C	114	114	114	114
Epoxy resin A	—	31.5	63	95
dibutyltin dilaurate	2	2	2	2
Silicon-containing flow agent	2.5	2.5	2.5	2.5
TiO ₂	138	151	163	175

Table 4
Powder Compositions IV (Examples 11 and 12)

Example	11 (comparison)	12
Polyester B	200	200
Isocyanate C	134	71
Epoxy resin A	—	63
dibutyltin dilaurate	2	2
Silicon-containing flow agent	2.5	2.5
TiO ₂	137	139

Table 5
Powder compositions V (Examples 13 and 14)

Example	13	14 (comparison)
Polyester D	200	200
Isocyanate C	40	—
Epoxy resin A	60	90
dibutyltin dilaurate	2	2
Silicon-containing flow agent	2.5	2.5
TiO ₂	125	125

Table 6
Powder compositions VI (Examples 15-17)

Example	15 (comparison)	16	17
Polyester D	200	200	200
Isocyanate D	62	62	62
Epoxy resin A	—	42	63
dibutyltin dilaurate	2	2	2
flow agent	2.5	2.5	2.5
TiO ₂	125	137	145

Table 7
Powder compositions VII (Examples 18 and 19)

Example	18	19
Polyester D	200	200
Isocyanate D	62	62
Epoxy resin B	9.5	14
dibutyltin dilaurate	2	2
flow agent	2.5	2.5
TiO ₂	130	130

Table 8
Powder compositions VIII (Examples 20-25)

Example	20 (comparison)	21	22	23 (comparison)	24	25
Polyester E	200	200	200	—	—	—
Polyester F	—	—	—	200	200	200
Isocyanate B	66	66	66	66	66	66
Epoxy resin A	—	42	63	—	42	63
dibutyltin dilaurate	2	2	2	2	2	2
flow agent	2.5	2.5	2.5	2.5	2.5	2.5
TiO ₂	125	135	145	125	135	145

Technical tests

The powder compositions shown in the preceding Tables were electrostatically sprayed on to phosphated sheet steel (Bonder 130, Registered Trade Mark) in a film thickness of 55 to 65 μ . The coated sheets were subsequently baked whereby the compositions melted to form smooth films and hardened. Three samples from each of the compositions of Examples 1 to 14 were prepared under different baking conditions, namely a) 30 minutes at 180°C, b) 30 minutes at 190°C, and c) 30 minutes at 200°C, and one sample from each of the compositions of Examples 15 to 25 was prepared by baking for 30 minutes at 200°C.

The coated sheets were subjected to the usual technical tests, the results of which can be seen from the following Tablets 9 and 10, which indicate the type of binder and the baking conditions used in the production of each sample.

Table 9

Example	1 (comp.)	2 (comp.)	3 (comp.)	4	5	6	7 (comp.)	8 (comp.)	9	10	11 (comp.)	12 (comp.)	13	14 (comp.)
Erichsen cupping test														
according to														
DIN 53 157 (mm)														
a)	1.2	4.5	7.5	6.5	9.0	8.0	4.0	4.9	4.4	3.5	3.0	5.0	6.0	0.5
b)	2.3	6.5	8.9	8.8	9.0	8.5	4.0	5.9	8.3	7.0	2.3	8.7	6.1	0.6
c)	5.1	7.5	8.0	8.4	—	8.3	4.7	4.7	8.6	7.4	4.5	9.0	7.7	9.0
Impact test according to														
ASTMD 2794-69,														
converted into kg.cm														
a)	<23.0	<23.0	>46.0	>46.0	>46.0	>23.0	<23.0	>46.0	>46.0	>36.8	<4.6	>4.6	>23.0	<4.6
b)	<23.0	<46.0	>46.0	>46.0	>46.0	>46.0	<23.0	>46.0	>46.0	>46.0	<4.6	>4.6	>23.0	<4.6
c)	<23.0	<46.0	>46.0	>46.0	>46.0	>46.0	<46.0	>46.0	>46.0	>46.0	<9.2	>36.8	>23.0	<9.2
Resistance to acetone *)														
a)											0	2	0	5
b)											0	1-2	0	5
c)											0	0-1	0	3-4

*)

0 = best value

5 = worst value

Table 10

Example	15 (comp.)	16	17	18	19	20 (comp.)	21	22	23 (comp.)	24	25
Erichsen cupping test according to DIN 53 157 (mm)	6.4	6.0	8.2	6.33	7.2	0.8	7.3	6.4	0.7	6.9	6.2
Impact test according to ASTMD 2794-69, converted into kg cm	<4.6	<13.8	<32.2	<36.8	<32.2	<4.6	<13.8	<13.8	<4.6	<13.8	<13.8
Resistance to acetone	0	1-2	1-2	0	0	1	1-2	1-2	1	1-2	1-2

Discussion of the results

As can be seen from Tables 9 and 10, the values for Examples 3 to 6, 8 to 10, 12, 13, 16 to 19, 21, 22, 24 and 26 all show a significant improvement in the Erichsen cupping test and the impact test values, compared with the corresponding values in the comparison Examples 1, 2, 7, 11, 15, 20 and 23, all of which were prepared without epoxy resin, and with the values in the comparison Example 14 which was prepared without polyisocyanate.

WHAT WE CLAIM IS:—

1. A coating composition which comprises a binder comprising a) a reaction product of a hardenable polyester and a partially blocked polyisocyanate (as herein defined) and B) an amount of up to 38.5 per cent by weight (referred to the total amount of component A) of an epoxy resin.
2. A composition as claimed in claim 1 wherein the polyester contains at least one hydroxyl group per molecule.
3. A composition as claimed in claim 1 or claim 2 wherein the polyester contains at least one trifunctional acid or alcohol component.
4. A composition as claimed in any one of claims 1 to 3 wherein the polyester contains from 10 to 60 mol % of at least trifunctional acid and/or alcohol components referred to the total molar amounts of acid and alcohol components respectively.
5. A composition as claimed in claim 4 wherein the mol % of at least trifunctional acid and/or alcohol components in the polyester is from 20 to 50 mol %.
6. A composition as claimed in any of the preceding claims wherein the polyester contains at least one mono-functional acid or alcohol component.
7. A composition as claimed in claim 6 wherein the polyester contains up to 30% by weight of monofunctional acid or alcohol components referred to the total weight of acid and alcohol components respectively.
8. A composition as claimed in claim 7 wherein the % by weight of monofunctional acid or alcohol components is up to 5% by weight.
9. A composition as claimed in any of the preceding claims wherein the polyester is based on terephthalic, phthalic or isophthalic acid or a combination thereof or a combination of one of these acids with adipic acid.
10. A composition as claimed in any of the preceding claims wherein the polyester has an acid number of less than 5.
11. A composition as claimed in claim 10 wherein the polyester has an acid number of less than 3.
12. A composition as claimed in any of the preceding claims wherein the polyester has a hydroxy number of from 50 to 250.
13. A composition as claimed in claim 12 wherein the polyester has a hydroxy number of from 100 to 220.
14. A composition as claimed in claim 12 wherein the polyester has a hydroxy number of from 130 to 200.
15. A composition as claimed in any of the preceding claims wherein the polyester has a melting point in the range from 60 to 90°C (as measured by the capillary method).
16. A composition as claimed in claim 15 wherein the polyester has a melting point in the range from 65 to 80°C (as measured by the capillary method).
17. A composition as claimed in any of the preceding claims wherein the melting viscosity of the polyester at 130°C is in the range from 100 to 7000 poise.
18. A composition as claimed in claim 17 wherein the melting viscosity of the polyester at 130°C is in the range from 100 to 1400 poise.
19. A composition as claimed in any of the preceding claims wherein at least one further synthetic resin containing hydroxyl groups selected from acrylic resins, vinyl polymers and polyurethane resins is incorporated into the binder.
20. A composition as claimed in claim 19 wherein the further synthetic resin containing hydroxyl groups is present in the form of the unreacted resin or the product of its preliminary reaction with the partially blocked polyisocyanate.
21. A composition as claimed in claim 19 or claim 20 wherein the molar proportion of hydroxy groups in the further synthetic resin is at most equal to the molar proportion of hydroxy groups in the polyester.
22. A composition as claimed in any one of the preceding claims wherein the polyisocyanate is at least partially blocked by a mono- or polyhydric phenol, a β -dicarbonyl compound, a carboxylic acid imide, a carboxylic acid amide, a sulphonamide, a mercapto compound or a lactam.
23. A composition as claimed in claim 22 wherein the polyisocyanate is at least partially blocked by ϵ -caprolactam.
24. A composition as claimed in any one of the preceding claims wherein there are 0.5 to 1.5 mol equivalents of free and blocked isocyanate groups in the polyisocyanate per mol equivalent of hydroxy groups in the polyester and, if present, in the further synthetic resin containing hydroxy

groups.

25. A composition as claimed in claim 24 wherein there are 0.6 to 1.35 mol equivalents of free and blocked isocyanate groups per mol equivalent of hydroxy groups.

26. A composition as claimed in claim 24 wherein there are 0.7 to 1.0 mol equivalents of free and blocked isocyanate groups per mol equivalent of hydroxy groups.

27. A composition as claimed in any one of the preceding claims wherein the epoxy resin has a melting point of at least 70°C (as measured by the capillary method).

28. A composition as claimed in claim 27 wherein the melting point of the epoxy resin is at least 100°C (as measured by the capillary method).

29. A composition as claimed in claim 27 wherein the melting point of the epoxy resin is at least 120°C (as measured by the capillary method).

30. A composition as claimed in any one of the preceding claims wherein the epoxy resin is based on diphenylolpropane.

31. A composition as claimed in any one of the preceding claims wherein there are 0.1 to 1.0 mol equivalents of epoxy groups in the epoxy resin per mol equivalent of free and blocked isocyanate groups in the polyisocyanate.

32. A composition as claimed in claim 31 wherein there are 0.2 to 0.8 mol equivalents of epoxy groups per mol equivalent of free and blocked isocyanate groups.

33. A composition as claimed in claim 31 wherein there are 0.3 to 0.7 mol equivalents of epoxy groups per mol equivalent of free and blocked isocyanate groups.

34. A composition as claimed in any one of the preceding claims which additionally contains at least one further ingredient selected from catalysts, pigments, fillers and flow agents.

35. A composition as claimed in claim 34 which additionally contains a catalyst to accelerate the addition of the polyisocyanate and/or epoxy resin to the hydroxy groups of the polyester and, if present, the further synthetic resin, and optionally pigments, fillers and flow agents.

36. A composition as claimed in any of the preceding claims which is a powder coating composition.

37. A composition as claimed in claim 36 wherein the maximum particle size of the composition is up to 100μ.

38. A composition as claimed in claim 36 wherein the particle sizes of the powder composition are from 50 to 70μ.

39. A coating composition substantially as herein described in any one of Examples 3 to 6, 8 to 10, 12, 13, 16 to 19, 21, 22, 24 and 25.

40. A process for the preparation of a coating composition as defined in claim 1 which comprises mixing a polyester containing free hydroxy groups with a partially blocked polyisocyanate in a first step and subsequently reacting an epoxy resin at a temperature of up to 130°C.

41. A process for the preparation of a coating composition as defined in claim 1 which comprises simultaneously mixing together a polyester, a fully blocked polyisocyanate, and an epoxy resin at a temperature of up to 130°C.

42. A process as claimed in claim 40 or claim 41 wherein the mixing of the epoxy resin with the reaction product of the polyester and the polyisocyanate or with the precursors thereof is effected at a temperature of up to 120°C.

43. A process as claimed in any one of claims 40 to 42 for the preparation of a powder coating composition wherein the mixture is subsequently cooled and converted to powder form.

44. A process for the preparation of a coating composition as defined in claim 1 substantially as herein described in Examples 3 to 6, 8 to 10, 12, 13, 16 to 19, 21, 22, 24 and 25.

45. A coating composition whenever prepared by a process as claimed in any of claims 40 to 44.

46. An article coated with a composition as claimed in any one of claims 1 to 39 and 45.

47. An article as claimed in claim 46 wherein the thickness of the coating is up to 250μ.

48. An article as claimed in claim 46 wherein the thickness of the coating is from 40 to 100μ.

49. An article as claimed in claim 46 wherein the thickness of the coating is from 50 to 80μ.

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